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Studies on the Coalescence of Liquid Droplets

Part III. The Influence of the Polarizing Potential on the Coalescence of Oil Phases in Aqueous Solutions

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The condition of coalescence of oil droplets in the aqueous phase was investigated. The experiment was carried out by modifying the apparatus of Cockbain *et al.* If the ionic surface active agent is contained in the oil phase, the coalescence of oil droplets was prevented at potentials higher than a certain value. This potential became small with increasing ionic strength of the continuous aqueous phase. This was similar to results on the coalescence of mercury droplets in the oil phase, which was prevented by the protection of the organic electrolyte. The adsorbed amount of the ionic surface active agent was found to be related to the critical potential of coalescence, so that the coalescence of oil droplets appeared to be prevented by the protection of the adsorbed layer of the agent, moreover, it was also concluded from the consideration of the orientation of surface active agents at the interface, that the protection was due to their polar groups.

I. INTRODUCTION

In the previous communication¹⁾ the condition of the coalescence of aqueous droplets in the oil phase was treated as a function of the interfacial potential and the composition of the system. It was found that, when the ionic surface active agent was contained in the oil phase, the coalescence of aqueous droplets was prevented by the electrostatic repulsion, while the coalescence took place when this repulsive force was weak. Moreover, if the oil phase contained the nonionic surface active agent, the coalescence of aqueous droplets was prevented by the protection of the adsorbed film. It was thus concluded that the same mechanism of stabilization prevailed the water in oil systems and the mercury droplets in aqueous solutions.^{2,3)}

In this paper the stabilization mechanism of oil droplets was investigated by examining the condition of the coalescence of oil phases in the aqueous solutions.

II. EXPERIMENTS

Materials

The solvent of the oil phase, MIBK, and water used were of the same purity as in the previous paper.¹⁾ Cetylpyridinium chloride (CPC) and sodium cetylsulfate (SCS) used as electrolytes of the oil phase, were of the Analar and Guaranteed

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Grade, respectively. KCl, KBr and KI used as electrolytes of the aqueous phase were of the Analar Grade.

Method

The condition of the coalescence of oil droplets in the aqueous phase was examined at first by using the same apparatus as before.¹⁾ However, oil droplets formed at tips of the glass capillaries, adhered to glass surfaces as soon as the droplets grew to moderate sizes, and then crept upwards along the capillaries. The same phenomena were found to take place, even if the glasses were treated with silicon or paraffin.

Therefore, this method was not feasible to the present system, and hence a new method was devised as shown in Fig. 1. This is essentially the same apparatus as that used by Cockbain *et al.*,⁴⁾ except that the potential difference can be applied to the system.

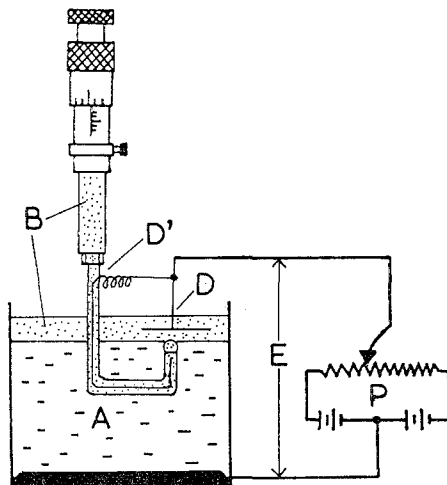


Fig. 1. The schematic diagram of the experimental apparatus.

An Agla micrometer syringe, equipped with a U-shaped glass capillary needle, was dipped in the aqueous phase A (15 ml) under the oil phase B (5 ml). The syringe contained the oil phase of the same composition as B. Now, the gap between the tip of the needle and the upper oil phase B was adjusted to a constant distance, 2 mm., by using the Shimadzu HV-50 cathethometer. An oil droplets of a constant volume, which was sufficient to fill the gap, was formed rapidly at the tip of the needle. Then, the time, required for the coalescence of the oil droplet and the upper oil layer to take place, was measured by the stop-watch.

The same potential difference E was applied to the platinum electrodes in the oil phase D and the glass capillary D', with reference to the mercury pool, by means of the potentiometer P. Here, the sign of E was conventionally taken as that of the aqueous phase with respect to the oil phase. The life time of the oil droplet was measured 10 to 20 times for each E , and the average life time was

Studies on the Coalescence of Liquid Droplets (III)

determined. Thus, the relation between t and E was obtained.

The electrocapillary curve was measured for each system. The detailed experimentation has already been reported elsewhere.⁵⁾

All measurements were carried out at the room temperature.

III. RESULTS

The effect of the KCl concentration in the aqueous phase on t vs. E and γ

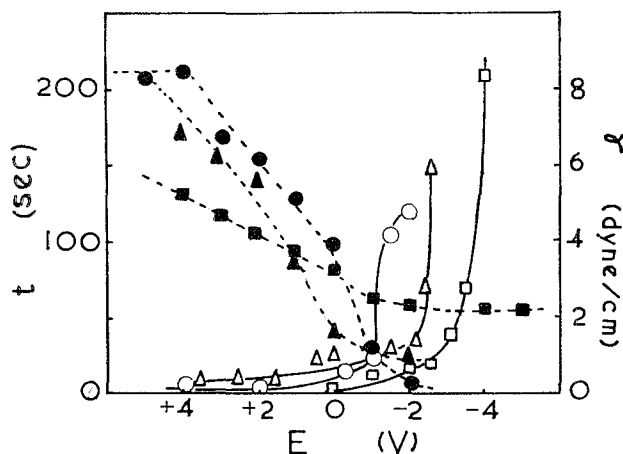


Fig. 2. The influence of the ionic strength in the aqueous phase on the coalescence of the oil droplet and γ vs. E curves.

—, t vs. E curves; ---, γ vs. E curves

Oil phase: 2.5×10^{-4} M CPC

Aqueous phase: \circ , \bullet , 1 M KCl; \triangle , \blacktriangle , 0.1 M KCl;

\square , \blacksquare , 1×10^{-2} M KCl

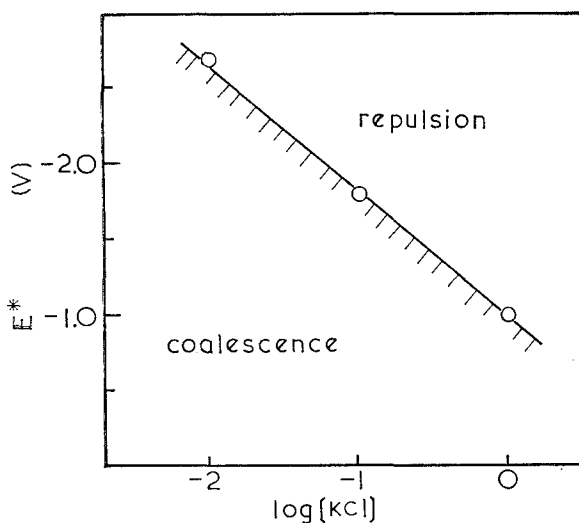


Fig. 3. The influence of the KCl concentration in the aqueous phase on the critical potential of coalescence of the oil droplet.

vs. E curves is shown in Fig. 2, for the KCl concentration 1 , 1×10^{-1} or $1 \times 10^{-2} M$, and the oil phase of $2.5 \times 10^{-4} M$ CPC in MIBK. The E value, at which the life time t begins to increase, shifts to a lower value when the KCl concentration increases. The linear increasing portion of t *vs. E* is extrapolated to zero life time, and the value of E at which it cuts the abscissa can be taken as the critical E value, E^* . The E^* value thus obtained is ca. $-1.0 V$ for $1 M$ KCl, ca. $-1.8 V$ for $1 \times 10^{-1} M$ KCl and ca. $-2.7 V$ for $1 \times 10^{-2} M$ KCl, respectively. The E^* *vs. log [KCl]* curve is shown in Fig. 3; a linear relation is obtained.

On the other hand, influences of the KCl concentration on the slope of electrocapillary curve, $d\gamma/dE$ for this system are almost the same for $1 M$ and $1 \times 10^{-1} M$, but the slope is small for the concentration higher than $1 \times 10^{-2} M$.

Figure 4 shows t *vs. E* and γ *vs. E* curves for aqueous phases containing $0.1 M$ KCl, KBr and KI, where the composition of the oil phase is the same as in Fig. 2. By the same extrapolation, the E^* value was determined. The value is ca. $-1.5 V$, $-3.0 V$ and $-4.0 V$ for KCl, KBr and KI, respectively. Thus, the electrolytes can be arranged in the order of absolute values of E^* by the following sequence: $KI > KBr > KCl$. The same sequence is also found for γ *vs. E* curves in this figure; this is the sequence of the increasing magnitude of the γ value.

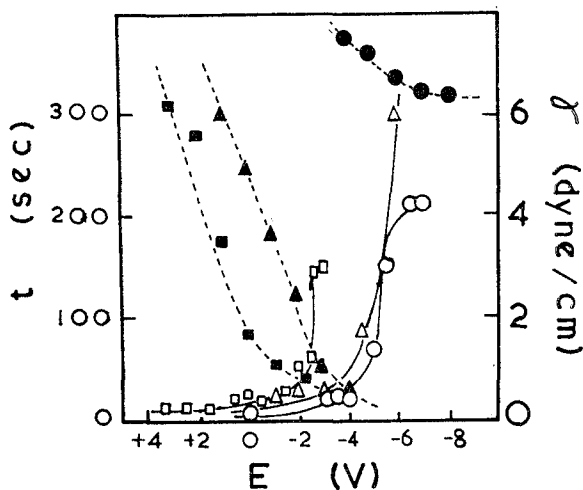


Fig. 4. The influence of halide ion species in the aqueous phase on the coalescence of the oil droplet and γ *vs. E* curves.

—, t *vs. E* curves; ·····, γ *vs. E* curves

Oil phase: $2.5 \times 10^{-4} M$ CPC

Aqueous phase: □, ■, $0.1 M$ KCl; △, ▲, $0.1 M$ KBr;

○, ●, $0.1 M$ KI

When the oil phase contains the anionic surface active agent, the t *vs. E* curve obtained is different from that for the cationic surface active agent. Figure 5 shows t *vs. E* and γ *vs. E* curves for the oil phase of $2.5 \times 10^{-4} M$ SCS in contact with the aqueous phase of $0.2 M$ KCl. The oil droplet in this system has a very large life time over the whole applied potential range, the time being

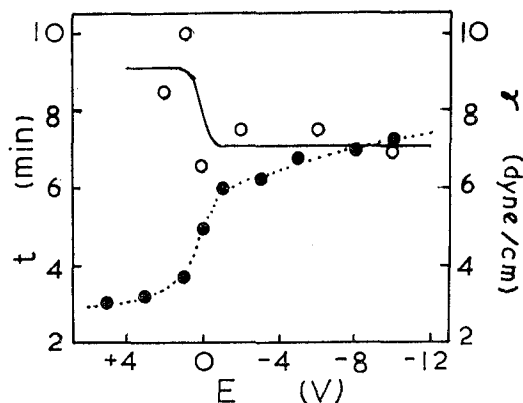


Fig. 5. The influence of the anionic surface active agent in the oil phase on the coalescence of the oil droplet and the γ vs. E curve.

—, t vs. E curve; ·····, γ vs. E curve

Oil phase: $2.5 \times 10^{-4} M$ SCS

Aqueous phase: ○, ●, $0.2 M$ KCl

several ten times of that for the oil phase containing the cationic surface active agent. It is clear from the γ vs. E curve in this figure, on the other hand, that the interfacial tension decreases with increasing E for $E < +1.0 V$, and then becomes constant at 3 dyne/cm for E higher this value.

IV. DISCUSSION

In experiments on the coalescence of mercury droplets in the aqueous or oil phase,^{2,3,6)} as well as of aqueous droplets in the oil phase,¹⁾ which have been reported already, the time of the drop growth was very short. These experiments, therefore, are concerned with the stabilization mechanism on droplets of short life time.

On the other hand, the life time of oil droplets measured by the present method, ranged from several ten seconds to several minutes. Hence, in order to discuss the stabilization mechanism by comparing the present result with previous ones, the consideration must be restricted to the short life time. Therefore, the value, E^* , at which the sharp increase in the life time of the present system begins to take place, must be compared with critical potentials for previous systems.

It has been stated already with regard to the system of aqueous droplets in the oil phase¹⁾ that, when the ionic concentration in the oil phase is lower than that of the aqueous phase, the electrical conductivity of the oil phase is low. It is supposed, then, that most of the applied potential difference drops in the oil phase owing to the high resistance.

Since, on the other hand, adsorbed surface active agent ions are orientated at the interface in a manner such that hydrophilic polar groups are directed towards the aqueous phase and hydrophobic groups towards the oil phase,^{7,8)} the electrostatic repulsion between polar groups is strongly influenced by the com-

position of the aqueous phase. Then, the adsorbed amount of surface active agent ions would be influenced by it^{9,10)}; the interfacial charge density, which depends on the adsorbed amount, would be affected by the electrolyte concentration in the aqueous phase. In fact, as can be seen from r vs. E curves in Fig. 2, the slope dr/dE increases with the increase in the KCl concentration. This shows that the surface charge density increases; the adsorbed amount of surface active agent ions increases.

If particles of hydrophobic sol or emulsion approach each other, the electrostatic repulsion occurs between them due to the overlap of double layers.¹¹⁾ This repulsion is governed among others by the ionic strength of the continuous phase and the surface charge density. In other words, the lower the ionic strength and the larger the surface charge density, the higher the electrostatic repulsion is. Therefore, it is not always true that, even if the surface charge density of droplets is high, the electrostatic repulsion between them is high, since the thickness of electrical diffuse double layer is small for high ionic strengths. The present result shows that the oil droplets are stabilized by the increase in KCl concentration.

Since the adsorption of surface active agent ions has been proved to increase with increasing KCl concentration, the coalescence of oil droplets would appear to be prevented by the protection of the adsorbed film rather than by the electrostatic repulsion. This protection is considered to be due to polar groups penetrated into the aqueous phase.

So far, the consideration has been made on the aqueous phase containing KCl. It is expected, however, that, when counterions having a strong affinity to polar groups of surface active agent ions, are contained in the aqueous phase, the protection of polar groups is influenced by the so-called counterion binding.^{7,8)} It is actually found in Fig. 4 that the larger the ionic radius of halide ions, the higher the absolute value of E^* is. Such a counterion binding gives rise to the disappearance of the ionic character of surface active agent and hence the neutralization of the surface charge density. Therefore, it is expected that halide ions showing strong counterion binding weaken the protecting action of polar groups of surface active agent ions.

Now, the coalescence of liquid droplets follows either of the following processes.¹²⁾ (I) The life time of liquid droplets is short in dilute solutions of surface active agents or in solutions of weakly surface active materials, and depends on the drainage time of the continuous phase between the droplets. In this case, the life time is strongly influenced by the electrostatic repulsion between them. (II) The life time is long in concentrated surface active agent solutions. In this case, the thinning of the liquid layer between droplets proceeds to a certain extent rapidly, after which the coalescence takes place due to the fluctuation. Therefore, the life time mainly depends on the stability of the interfacial film.

It was reported that, for systems of aqueous droplets in the oil phase¹⁾ as well as mercury droplets in the aqueous phase containing inorganic electrolytes,²⁾ the stabilization against coalescence of droplets is governed by the electrostatic repulsion. Hence, the process of coalescence of these systems can be explained

by the process *I*. On the other hand, the protection found in systems of mercury droplets in the aqueous phase³⁾ and non-aqueous solutions containing surface active materials,⁴⁾ as well as of aqueous droplets in the oil phase containing the nonionic surface active agent,¹⁾ can be explained by the process *II*. Then, it is considered for the system of the oil droplets in the aqueous phase in the present paper that, since the coalescence is prevented by polar groups of cationic surface active agents adsorbed at the oil-water interface, this corresponds to the process *II*.

This process is also found in the system in which the anionic surface active agent was added to the oil phase. For instance, in Fig. 5, the life time of the oil droplets is large over the entire region of applied potential difference; the life time is of the order of several minutes. This is explained by the fact that an anionic surface active agent can easily bind to the counterion. Actually, in the system of Fig. 5, the interfacial tension is constant for $E > +1.0 V$, and a whitish insoluble film is formed at the oil-water interface for $E > +3.0 V$. It appears, therefore, that the stabilization process is due to the same protection as in the case of the oil droplets of a short life time. However, it is not the polar group of the surface active agent, but the insoluble film produced by the counterion binding, which gives rise to these protection.

Discussions of the present papers are rather qualitative, for the real polarizing potential at the oil-water interface and ionization constant in the oil phase, which is necessary for the quantitative study, has not been determined.

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